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Dielectric properties of antimony trioxide films*

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Sb_2O_3 film capacitors (Al/Sb_2O_3/Al) have been studied in details for their dielectric behaviour at different temperatures (78–380°K) and frequencies (10^2–10^5 Hz). Dielectric constant was thickness dependent for thinner films but became independent (8.2) for thicker films ($>$ 800 Å). Loss factor (tan δ) (about 0.003) at 1000 Hz was found to be independent of film thickness. Capacitance, though dependent on temperatures and frequencies, became invariant with the frequency at low temperatures. Loss factor showing a pronounced minimum (tan δ_{min}) in the frequency spectrum increased with temperatures and tan δ_{min} shifted to the higher frequency region. Breakdown field strength followed the Forlani-Minnaja relation $F_B \alpha d^{-\frac{1}{2}}$. These capacitors had high stability, and low TCC and loss factors. The a.c. behaviour of these capacitors especially tan δ_{min} and its variation have adequately been explained from a capacitor model proposed previously by us.

1. Introduction

Dielectric films are extensively used in optical and electrical devices and also as film capacitors in microelectronic circuits. The latter applications, however, require amongst others high resistivity and dielectric field strength, low loss factors and TCC, and a near frequency invariant capacitance. Only a few oxide films, however, fulfil these requirements. A.C. properties of several films including some rare earth oxides have recently been studied by us (Goswami & Goswami 1973, 1974*a*, 1974*b*). The bulk antimony trioxide has been reported to have high electrical resistivity as well as energy band gap (Korzh *et al* 1969, Wood *et al* 1972). A detailed study has therefore been made on the dielectric behaviour of the evaporated films. Studies on the optical properties of these films have already been reported by us (Goswami & Goswami 1974*c*).

2. Experimental

Pure antimony trioxide powder (Sb_2O_3) white in colour (supplied by M/s Sujachome Export, Moscow, USSR) was placed inside a conical silica boat which was heated by a tungsten filament and the powder was initially degassed in vacuo (10^{-5} mm of Hg) for about half an hour at a low heat. The temperature of the

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boat was then raised and the deposition of the oxide films was made through appropriate masks at room temperature on glass substrates in the manner described previously by us (Goswami & Goswami 1973, 1974*b*). A set of samples of varying thickness were prepared in each evaporation and many such sets were made for measurements.

Thick aluminium deposits were used both as base and as counter electrodes for the fabrication of the capacitors comprising of $Al/Sb_2O_3/Al$ system. These were then aged at room temperature for several days and subjected to annealing by repeated heating (about 110°C) and cooling cycles in vacuo. This stabilisation was essential for reproducible measurements. Capacitance (C), loss factor ($\tan \delta$) were measured in vacuo at different frequencies (10^2–10^5 Hz) and temperatures (78–380°K) using a Marconi universal bridge (model TF 2700) in the manner described previously by us (Goswami & Goswami 1973, 1974*b*). The breakdown voltage (V_B) was also measured and the dielectric field strength (F_B) estimated. Multiple beam interferometry method was used for measuring the film thickness. Unless otherwise stated, the measurements were generally carried out at room temperature at 1 kHz frequency. Dielectric constant (ϵ) was evaluated from the knowledge of capacitance, film thickness and the effective capacity area.

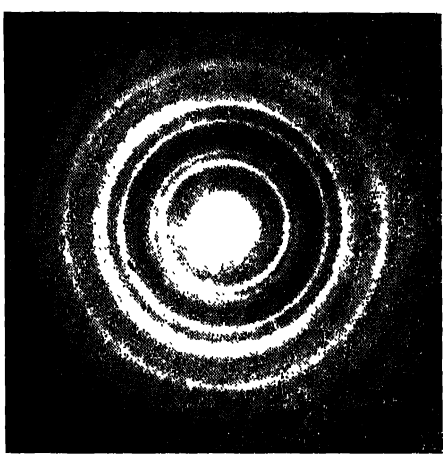

Fig 1. Electron diffraction pattern of polycrystalline Sb_2O_3 film.

In order to identify the nature of the dielectric films, the deposition was also made on polycrystalline sodium chloride tablets at room temperature. These were examined by the transmission electron diffraction method. Figure 1 shows a typical polycrystalline pattern of the deposits which conforms to the normal fcc structure of the Sb_2O_3 films ($a = 11.3$ Å).

3. Results

(i) *Ageing and annealing effects* :

$Al/Sb_2O_3/Al$ films capacitors showed little ageing effect with time when kept in vacuo. But when subjected to cyclic heating and cooling in vacuo as mentioned earlier capacitance decreased only slightly and attained stability within a short period. The loss factor was generally low (0.003) and did not significantly change on annealing.

(ii) *Effects of film thickness* (d) :

Variations of capacitance (as measured at room temperature) and dielectric constant with the film thickness are shown in figure 2, where C and ϵ (log scale) are plotted against $1/d$. It is seen that although capacitance decreased with the increase of film thickness the proportionality law i.e., $C \propto 1/d$ was valid for thicker films (say $>$ 700 Å) only and for thinner films this was not true. This

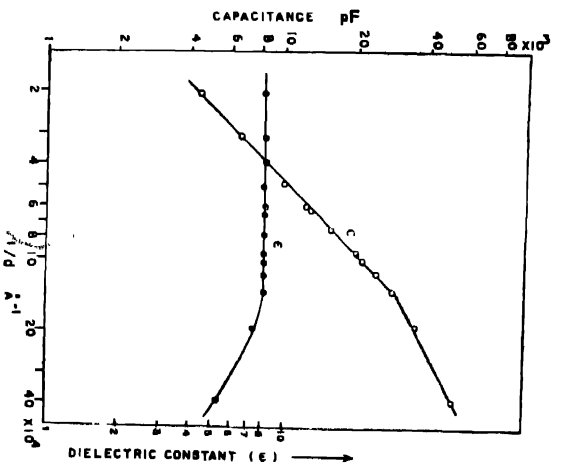

Fig. 2. Variation of C and ϵ with $1/d$.

is more clearly seen from the dielectric constant graph where ϵ increased from 5 to 8.2 for the film thicknesses ranging between 250–700 Å and remained invariant for all thicker films. Tan δ was low (< 0.003) and remained independent of d. This behaviour was similar to those of zinc sulphide and praseodymium film capacitors reported earlier (*loc. cit*).

(iii) *Frequency and temperature effects on τ and tan δ* :

A typical variation of capacitance with the frequency ($f = \omega/2\pi$) for a film thickness about 1580 Å at different temperatures is shown in figure 3. It is seen that capacitance decreased with the increase of the applied frequency and this variation was more at higher temperatures and lower frequencies. With the decrease of temperature C became reduced and eventually was independent of

the frequency near the liquid nitrogen temperature region. This trend was observed for all film thicknesses (250–5000 Å) studied by us. The curves show the corresponding ϵ at different temperatures and frequencies. It is interesting to note that at low temperatures ϵ was about 8.05 for all frequencies compared to 8.2 at 1 kHz at room temperature.

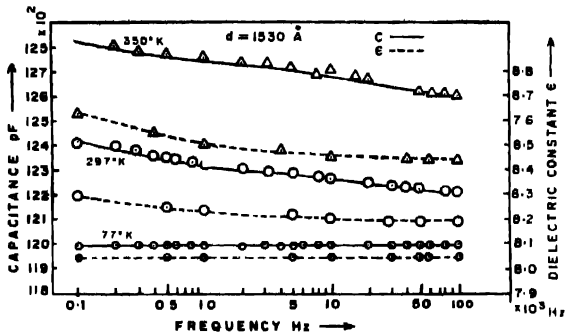

Fig. 3. Variation of C and ϵ with frequency (f) at different temperatures; $d \approx 1580$Å.

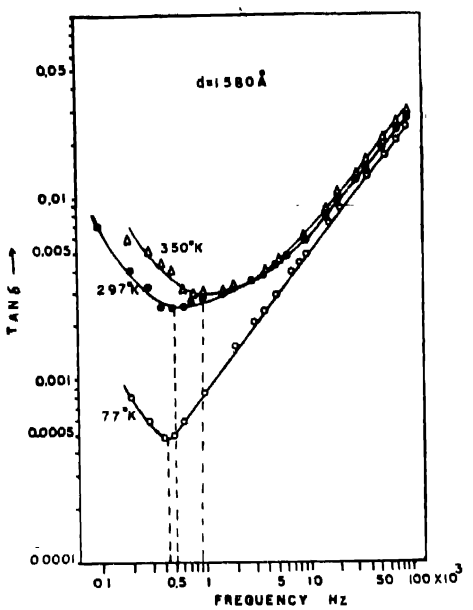

Fig. 4. Variation of tan δ with frequency at different temperature; $d \approx 1580$Å.

The influence of frequency and temperature on the loss factor is shown in figure 4. Tan δ shows a minimum value as a function of frequency. This tan δ_{min} occurred at a frequency f_{min} (or ω_{min}) depending on the temperature and other factors to be discussed later on. The position of f_{min} and hence tan δ_{min} shifted

to the frequency region with the rise of temperature and *vice versa*. Both tan δ and tan δ_{max} increased with the rise of temperature. The above features in the loss factor curves were true for all thicknesses of Sb_2O_3 film capacitors.

(iv) *Breakdown voltage* (V_B) *and dielectric field strength* (F_B) :

As expected the breakdown voltage increased from 2V to 9 V with the increase of film thickness from 260–3000 Å whereas the field strength decreased from 9.6 to 6.9×10^5 V/cm (table 1). When F_B was plotted against d (log-log scale) the graph (figure 5) showed two distinct linear regions. Thicker films (> 700 Å) showed a negative slope (0.5) thus obeying the Forlani-Minnaja law ($F_B \propto d^{\frac{1}{2}}$) whereas for the thinner films the curve was practically parallel to the d-axis.

Table 1. Variation of breakdown voltage (V_B) and dielectric field strength (F_B) with film thickness

Thickness (d) Å	Breakdown voltage (V_B) volts	Dielectric field strength (F_B) volts/cm
260	2.5	9.5×10^5
520	5.0	9.6×10^5
740	6.8	9.4×10^5
850	7.2	8.5×10^5
1050	8.0	7.5×10^5
1300	9.0	6.9×10^5

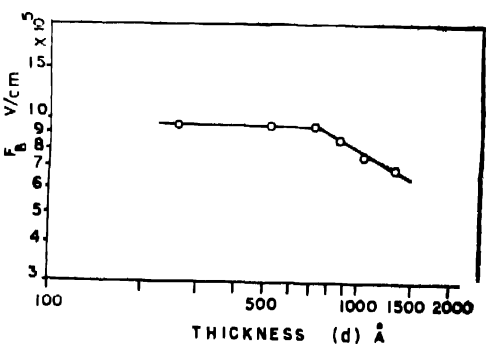

Fig. 5. Variation of F_B with thickness (d); slope = −0.5.

(v) *TCC and* $\Delta C/C$:

Two other parameters which are of great importance for practical applications as capacitor films are the temperature coefficient of capacitance (TCC) and the percentage variation of capacitance with frequency normalised at an

arbitrary frequency ($\Delta C/C\%$). The variation of capacitance with temperature for different film thicknesses (900 to 3200 Å) at 1 kHz is shown in figure 6. It is seen that TCC is generally low (< 100 ppm/°K) for thicker films and decreases further in the lower temperature region. Thinner films, however, have a slightly higher TCC (200–600 ppm/°K).

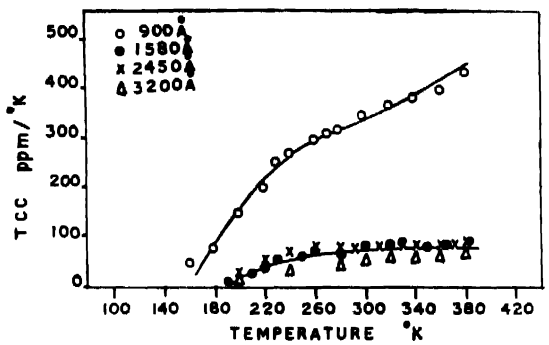

Fig. 6. Variation of TCC with d.

The variation of capacitance at room temperature with the applied frequency normalised at 1 kHz is shown in figure 7. It is seen that below 1 kHz this is positive, and above this it is negative. However, $\Delta C/C$ was small ($< 0.8\%$) and more or less independent of film thickness.

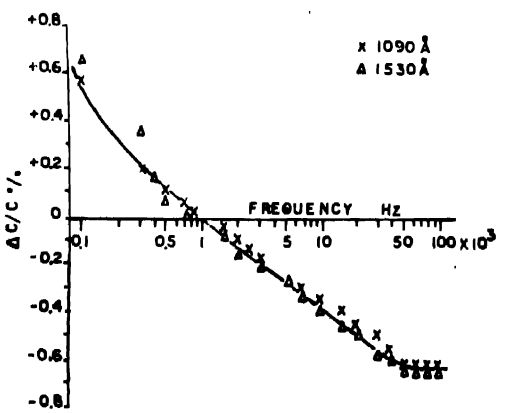

Fig. 7. Variation of $\Delta C/C$ with frequency.

4. Discussion

Dielectric properties of thin films have been investigated by a number of workers. Recent studies on the a.c. behaviour of film capacitors at a wide range

of frequencies and temperatures including low temperatures showed two characteristic features viz., (*a*) a loss peak in tan δ vs. frequency curves at different temperatures and a thickness dependent dielectric constant (Nadkarni *et al* 1970, Goswami *et al* 1974*b*) and (*b*) a pronounced loss minimum in tan δ vs frequency curves at all temperatures together with a thickness independent dielectric constant except for very thin films (Goswami *et al* 1973, 1974*a*). Simmons *et al* (1970), assuming the presence of two additional barrier layers (Schottky barriers) at the two dielectric-electrode interfaces, made predictions which agreed rasonably well with the experimental observations, such as loss peak, etc. in *a*-type of films. The dielectric behaviour of the (*b*) type of film capacitors has recently been explained by us (Goswami *et al* 1973, 1974*a*) from a model comprising of a capacitor element (C) invariant with frequency and temperature in parallel with a dielectric resistive element (R) and in series with a small lead resistance (r) where $r << R$. The above model of ours predicts almost all the basic characteristics observed for zinc sulphide and praseodymium oxide film capacitors and the important conclusions derived from our theory (Goswami & Goswami 1973) are summarised below for comparisons.

(i) Loss factor (tan δ) at any frequency is related to C, R and r by the equations

$$\tan \delta = (1/\omega)RC + \omega rC + (r/\omega)R^2C. \quad \ldots (1)$$

Since $r << R$,

$$\tan \delta = (1/\omega)RC + \omega rC. \quad \ldots (2)$$

At low frequencies the above reduces to

$$\tan \delta = 1/\omega RC \quad \ldots (3)$$

and at high frequencies

$$\tan \delta = \omega rC. \quad \ldots (4)$$

Thus the loss factor is directly or indirectly proportional to the frequency at different frequency regions.

(ii) Tan δ_{min} occurring at a particular frequency (ω_{min}) is given by the equation

$$\omega_{min} = 1/(rRC^2)^{\frac{1}{2}}. \quad \ldots (5)$$

Since R is related to the temperature by the equation $R = R_0 \exp \Delta E/kT$, where ΔE is the activation energy, R will decrease with the increase of temperature. Hence by the eq. (5) ω_{min} will shift to the higher frequency region.

(iii) Series capacitance (C_S) at any temperature and frequency is given by the equation

$$C_S = C(1+1/\omega^2R^2C^2). \quad \ldots (6)$$

Now at low temperatures and at high frequencies, R and $\omega^2R^2C^2$ will be large and hence

$$C_S = C. \quad \ldots (7)$$

Thus C_S will be invariant with frequency.

Comparing the a.c. behaviour of Sb_2O_3 film capacitors it is seen that the variation of capacitance with the frequency at different temperatures is explained from eqs. (6) and (7). Eqs. (3), (4) and (5) explain the different features of tan δ vs. frequency curve and also the significance of tan δ_{min}. The shift in ω_{min} and tan δ_{min} with the increase of the temperature is also explained. At high frequencies the rise of tan δ governed by eq. (4) requires the lead resistance (r) to be independent of frequency and temperature. The estimated values of r from tan δ vs. frequency measurements at differnt temperatures have been found to be very close to those obtained by actual measurements ($\approx$2.1Ω).

Both tan δ and tan δ_{min} increase with the temperature due to the increase of conductivity of the dielectric layers at higher temperatures. TCC is, therefore, positive. The low dissipation loss seems to be associated with the high dielectric resistance (R) of the deposited layers. The calculated value at room temperature obtained from eq. (3) and that estimated from ω_{min} position from eq. (5) were found to be of the same order ($\approx 10^7$ Ω). The resistivity of Sb_2O_3 films was, therefore, about 10^{11}–12^{12} ohm cm which was close to that of the bulk value (about 10^{11} ohm cm) reported by Korzh *et al* (1969).

The dependence of dielectric constant on d in the thin film region can be attributed to the defects, chiefly voids, present invariably in vapour phase deposits Goswami & Goswami (1973). For thicker films these voids are effectively filled up and hence ϵ attained a constant value close to that of the bulk. It is also interesting to note that the Forlani-Minnaja relation holds good for thicker films only.

Optical properties of the Sb_2O_3 films have also been studied by us (Gowami & Goswami (1974*c*). These films had high refractive indices ($n \approx$ 1.90 to 1.97) and practically no absorption in the visible regions except for very thick films ($\approx$ 10,000 Å) at lower wavelengths ($<$ 4000 Å). The optical dielectric constant ($= n^2 \approx 4$) was nearly half the observed value (8.2) at 1 kHz at room temperature (cf. figure 2). Hence remaining half must have arisen from the contributions from atomic (including ionic), dipole orientational or interfacial polarisations. As there was no peak in the tan δ graph at low temperatures as well as at low frequencies, the contributions from the last two factors would hence be absent.

Since the measurements of C at liquid nitrogen temperature region would suppress the contribution of ionic polarisation to ϵ and also because there was no significant variation of ϵ measureed at 1 kHz at room temperature from the dielectric constant at low temperature, it may be concluded that the remaining half was the contribution primarily from the atomic polarisation.

The above study of the a.c. behaviour of Sb_2O_3 films clearly shows that the model adopted by us for zinc sulphide and praseodymium oxide films is also applicable in the present case. Further, because of low dissipation lossses (< 0.003), low TCC (< 100 ppm/°K), high breakdown field strength (7×10^5 V/cm) and practically frequency invariant capacitance, Sb_2O_3 films appear to be good dielectric materials for several applications.

References

Forlani F. & Minnaja N. 1964 *Phys. Stat. Solidi.* **4**, 311.
Forlani F. & Minnaja N. 1969 *J. Vac. Sci. Technol.* **6**, 518.
Goswami A. & Goswami Amit P. 1973 *Thin Solid Films* **16**, 175.
Goswami A. & Goswami Amit P. 1974*a* *Thin Solid Films* **20**, S3.
Goswami Amit P. & Goswami A. 1974*b* *Indian J. Pure Appl. Phys.* **12**, 26.
Goswami A. & Goswami Amit P. 1974*c* *Thin Solid Films* **20**, S33.
Korzh P. D. & Gulayeva G. P. 1969 *Fiz. tekh. Popuprov.* **3**, 782.
Nadkarni G. S. & Simmons J. G. 1970 *J. Appl. Phys.* **41**, 545.
Simmons J. G., Nadkarni G. S. & Lancaster M. C. 1970 *J. Appl. Phys.* **41**, 538.
Wood C., Van Pelt B. & Dwight A. 1972 *Phys. Stat. Solidi.* **b54**, 701.